PATENT APPLICATION

PLASMA DETEMPLATING AND SILANOL CAPPING OF POROUS DIELECTRIC FILMS

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PLASMA DETEMPLATING AND SILANOL CAPPING OF POROUS DIELECTRIC FILMS

CROSS-REFERENCE TO RELATED APPLICATIONS

5   This application is a continuation-in-part claiming priority under 35 USC 120 from US Patent Application No. 10/404,693 filed March 31, 2003 by Humayun, et al., and titled "METHOD FOR FORMING POROUS FILMS BY POROGEN REMOVAL COMBINED WITH IN SITU SURFACE MODIFICATION." This application is incorporated herein by reference for all purposes.

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FIELD OF THE INVENTION

This invention relates to methods for preparing porous films using porogen technology. More specifically, the methods involve providing a precursor film comprising porogen and a dielectric matrix and removing the porogen and protecting silanol groups within the dielectric matrix using plasma techniques. The resulting material can be used as a low-k dielectric film in integrated circuits.

BACKGROUND OF THE INVENTION

Discovering ways to minimize the resistance-capacitance (RC) delay of metal interconnects is a primary pursuit within the high performance integrated circuit manufacturing industry. The RC delay is the time it takes a signal to propagate through a metal interconnect as a result of the resistance of the metal lines and the capacitance of the surrounding dielectric. Reducing the RC delay increases the speed of the signal propagation, thereby improving the performance of a device. One approach to reducing RC delay is by using lower resistance metals; for example, copper instead of aluminum. Another approach to reducing RC delay is by reducing the capacitance of the surrounding dielectric by using a material with a low dielectric constant, k.

The dielectric constant, k, is an intrinsic property of a material, which determines the electrostatic energy that can be stored within the material. The numerical value k is defined relative to a vacuum, for which k = 1, exactly. In IC applications, "low-k" dielectrics are conventionally defined as those materials that have k < ~ 4. This low-k definition comes from the k value of SiO_2, the traditional primary IC dielectric material, which has k ≈ 4. Since current technologies involving smaller features sizes are requiring k < 4, efforts have been focused on finding materials with lower k than that of SiO_2.

One widely used means of obtaining a low-k dielectric material is by incorporating carbon or hydrocarbons into a SiO_2 material. Since most hydrocarbons have a lower k than SiO_2, the resulting carbon-incorporated material has an overall lower k than pure SiO_2 – typically between 3.1 and 2.5, depending on the amount of carbon added and the type of organic precursor that is used. However, as IC features continue to decrease to smaller and smaller sizes, there is a drive to find materials with even lower k than can be obtained by using the carbon-incorporated SiO_2 alone.

Currently, the only known way to obtain a usable dielectric with k < 2.5 is by using techniques to produce pores or voids in a dielectric material with a dielectric constant k ≈ 2.5 to 4. Since the dielectric constant for air is only slightly higher than that of a vacuum, the resulting porous dielectric will have a significantly decreased k. A common technique for fabricating porous dielectric materials involves the formation of a composite film consisting of two components: a porogen (an organic material, typically a polymer) and a silicon-based dielectric. Once the composite film is formed onto the substrate, the organic porogen component is removed, leaving a porous silicon-based dielectric matrix.

There are significant challenges, however, associated with forming a porous dielectric material, particularly in the porogen removal process. A standard technique for porogen removal involves heating the wafer for several hours to thermally degrade and remove the porogen. Another technique involves exposing the wafer to a plasma treatment while heating the wafer. This porogen removal process creates "dangling bonds" (unsaturated SiO- or Si- groups) within the silicon-based dielectric matrix, which when exposed to ambient conditions, will react with moisture to create hydroxyl groups. These hydroxyl groups will in turn adsorb more moisture from the ambient to add water to the silicon-based dielectric matrix. Unfortunately, since water has a dielectric constant of about 80, this significantly increases the overall dielectric constant for the film.

What are needed therefore are improved methods for forming low k dielectric materials for integrated circuits.

SUMMARY OF THE INVENTION

The present invention addresses these needs by providing improved methods of preparing a low-k dielectric material on a substrate. The methods involve providing a precursor layer comprising a hydrocarbon porogen in a dielectric matrix and exposing the precursor layer to a plasma having a silanol capping agent to remove the porogen to create voids within the dielectric matrix and concurrently protect the dielectric matrix with hydrophobic protecting groups. Porogen removal and silanol capping may be performed contemporaneously or sequentially. If performed sequentially, silanol capping is performed without first exposing the dielectric matrix to moisture or ambient conditions.

In one embodiment, the methods include the following sequence of operations: (a) providing a precursor layer on said substrate, said layer comprising an organic porogen in a dielectric matrix; and (b) exposing the precursor layer to a plasma comprising a silanol capping agent provided therein to remove said porogen from the precursor layer to create voids within the dielectric matrix and concurrently protect the dielectric matrix with hydrophobic protecting groups. In another embodiment, the methods include (a) providing a precursor layer on said substrate, said layer comprising an organic porogen in a dielectric matrix; and (b) exposing the precursor layer to a plasma to thereby remove said porogen from the precursor layer to create voids within the dielectric matrix; and (c) after removing said organic porogen, exposing the dielectric matrix to a silanol capping agent, without first exposing the dielectric matrix to moisture or ambient conditions. In some embodiments, after (a), the precursor layer is exposed to ultraviolet radiation to remove at least a portion of the porogen before (b).

The precursor layer is formed by chemical vapor deposition, plasma-enhanced chemical vapor deposition, a print on process, dip casting, a spin on process, a spray on process or supercritical dielectric infusion in polymer matrix. In some embodiments, the porogen in the precursor layer is a hydrophobic phase of a block copolymer. In preferred embodiments, the dielectric matrix comprises silicon and oxygen, more preferably silicon, oxygen, carbon, and hydrogen. In specific embodiments, the dielectric matrix is derived from at least one of TEOS and MTEOS.

Any suitable capping agent can be used. In some embodiments, the silanol capping agent comprises one or more of a silane amine, a disilazane, a chlorosilane, an aldehyde, an alkylsiloxane and an alkyl alkoxysilane. In preferred embodiments, the silanol capping

agent comprises one or more of hexamethyldisilazane (HMDS), dimethyldimethoxysilane (DMDMOS), trimethylchlorosilane, and an acetaldehyde.

To remove the porogen, the plasma comprises either a reducing gas, such as at least one of hydrogen, ammonia, carbon monoxide and methane, or an oxidizing gas, such as at least one of carbon dioxide, nitrous oxide and oxygen. The plasma may also include nitrogen or unreactive gases such as at least one of nitrogen, argon or helium on their own or as carrier gases. In one approach, the substrate and precursor layer remain under vacuum during the porogen removal and silanol capping operations, and at all times in between. This may be accomplished by performing the removal and capping operations at different stations in a multistation tool.

The precursor films may be either exposed directly to the plasma such as by using a planar or barrel type reactor or the films may be exposed to downstream plasma to prevent direct ion bombardment of the film. The plasma may be generated by a high or low frequency source or may be generated by a combination of high and low frequency source(s).

In embodiments wherein the porogen removal and silanol capping occur concurrently, the silanol capping agent may be introduced to the plasma using a carrier gas. In other embodiments, no carrier gas is used. The plasma source power, substrate temperature, dosage of silanol capping agent, chamber pressure and exposure times will vary depending upon plasma reactor set up and plasma composition. Typical plasma source powers range between about 100 and about 2000 Watts. Typical substrate temperatures during plasma exposure ranges between about 100 and about 400 degrees Celsius. In one embodiment, the flow rate of silanol capping agent provided in the plasma range between about 0.2 and about 20 ml/minute and preferred chamber pressures range between about 1 and about 10 Torr. Typical plasma exposure time ranges between about 5 seconds and 20 minutes.

In embodiments wherein the porogen removal and silanol capping occur sequentially, the dielectric matrix can be exposed to the silanol capping agent by way of one of a vapor phase, liquid phase, supercritical phase or plasma phase. In preferred embodiments, the silanol capping agent is provided in a second plasma. If provided in a second plasma, the silanol capping agent may be provided with or without a carrier gas. The carrier gas may comprise a reducing gas such as those produced by adding at least one of hydrogen, ammonia, carbon monoxide and methane. Alternatively, the carrier gas may comprise an oxidizing gas such as at least one of carbon dioxide, nitrous oxide and oxygen. Additionally,

at least one of nitrogen, argon or helium may also be used as the carrier gas. The second plasma source power, substrate temperature, dosage of silanol capping agent, chamber pressure and exposure times will vary depending upon plasma reactor set up and plasma composition.

5   These and other features and advantages of the invention will be described in detail below with reference to the associated drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

The following detailed description can be more fully understood when considered in conjunction with the drawings in which:

Figures 1A and 1B are flowcharts summarizing the stages of two preferred embodiments of the invention.

Figure 2 shows a plasma system that may be used to perform operations in accordance with some embodiments of this invention.

Figure 3 is a composite figure of FTIR spectra of mesoporous silica films before and after various treatment methods in accordance with the invention.

Figures 4 is a graph showing the amount of damage to the dielectric backbone of a porous film as a result of using a H_2/N_2 plasma compared to using CO_2 plasma.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

INTRODUCTION

In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present invention, which pertains to porogen removal and "silanol capping" treatment during formation of a porous dielectric material. The present invention may be practiced without some or all of these specific details. In other instances, well known process operations have not been described in detail to not unnecessarily obscure the present invention. While the invention will be described in conjunction with the specific embodiments, it will be understood that it is not intended to limit the invention to the embodiments.

For many embodiments of the invention, the substrate is a semiconductor wafer. A semiconductor wafer as discussed in this document is a semiconductor substrate at any of the various states of manufacture/fabrication in the production of integrated circuits. The terms "wafer," "substrate," "semiconductor wafer," and "wafer substrate" are used interchangeably herein. It is noted, that the invention is not limited to semiconductor wafers. For example, these methods may be used for treating mesoporous molecular sieves.

The present invention involves forming a low k dielectric material by way of a "precursor layer" that contains both a porogen and a dielectric matrix formed in regions around the porogen. During methods of this invention, the porogen is removed from the precursor layer to create a low-k dielectric layer. Within the precursor layer, the porogen resides in locations that will subsequently become void locations in the final dielectric layer. Hence, the porogen and dielectric matrix typically exist as separate phases within the precursor layer. To some degree, the porogen defines the porosity, void volume, tortuosity and other parameters characterizing the pore morphology in the final low-k dielectric material. In some cases, the pore morphology is set before the porogen is removed. In other cases, it is set during the porogen removal process. Further, the dielectric matrix may assume its final composition and structure either before or during the porogen removal process. A precursor layer may be formed by any one of many different techniques including spin-coating processes, supercritical infusion into a polymer matrix, print-on, dip coating, and chemical vapor deposition – particularly plasma enhanced chemical vapor deposition (PECVD).

Generally, a porogen is any removable material that defines void regions in a dielectric matrix. In the case of an ordered porous or mesoporous dielectric matrix, the porogen is frequently referred to as a "template." In many cases, the porogen comprises an organic material. Its properties depend upon the means by which it is removed from the precursor layer. Porogens are commonly removed from the precursor layer by decomposition, volatilization, and/or solvation. Thus, some porogens are highly volatile at elevated temperatures. Others are soluble in particular solvents. Still others are readily decomposed by heat, plasma, radiation, e-beam, microwave etc.

In one important dielectric formation process, the porogen is a block copolymer having chemically distinct components that segregate into separate phases. For example, block copolymers may be structured such that long range ordered hydrophilic and hydrophobic phases are formed within the film by amphiphilic self-assembly. One example of such a polymer is a block copolymer of PEO polyethylene oxide and PPO polypropylene oxide. If such block copolymers are used, a hydrophilic catalyst and dielectric precursor (e.g., TEOS) preferentially segregate into the hydrophilic regions (i.e., the PEO regions) where the dielectric precursor reacts to form dielectric. After removal of the porogen, an ordered porous dielectric matrix is left. The ordered structure of the porous film is dictated by the relative amounts of PEO and PPO.

Techniques for forming ordered mesoporous layers will be described further. Note that the invention is not limited to mesoporous layers of this type. For example, the present invention can be employed with non-ordered porous precursor layers, having pores of various sizes. Note that according to the International Union of Pure and Applied Chemistry (IUPAC), mesoporous materials are defined as those with pore diameters between 2 nm and 50 nm. The present invention, however, is not limited to this strict definition of mesoporous material in that porous materials having pores of any size may be formed. As such, the term "mesoporous" as used herein will refer broadly to porous materials having any pore size. In a number of embodiments, typical mesoporous materials will have pore diameters ranging between about 0.5 nm and about 50 nm.

Further, the invention is not limited to silicon dioxide dielectric materials. It can be used to produce a wide variety of silicate materials to carbon-containing dielectrics, for example. The invention can also be used to produce porous metal containing materials such as metal oxides.

MESOPOROUS PRECURSOR LAYERS

In one example, the process chemistry for creating a mesoporous precursor layer employs four reagents to form a mesoporous precursor layer. These are (a) a template-forming precursor (e.g., a surfactant type block copolymer), (b) a silica-forming precursor such as TEOS (tetraethyl orthosilicate), (c) a solvent such as water and/or ethanol, and (d) a catalyst such as an acid to help drive the reaction. Many common spin-coat techniques involve mixing all the reactant components together and spin-coating the mixture onto the substrate in one process step. Solution spreading, drying, block copolymer segregation, and silica formation take place all at once. Other methods, such as those described in previously referenced United States Patent Application number 10/295,965, involve a two-step process in which the template-forming precursor, solvent and catalyst are mixed and applied by spin-coat or print-on methods to form the template in a first process step, then the silica-forming precursor is introduced to the formed template in a second process step. In one embodiment, the silica-forming precursor is introduced in the form of a supercritical fluid (e.g. TEOS dissolved in CO_2) so that it can readily infuse into the hydrophilic void regions of the formed template.

Many variations on the basic process are possible. Some of these will now be described briefly. In one example, a field generator is employed during the deposition process to apply an electric field to align electrostatic domains and/or ordered structures (e.g., micelles) within the precursor layer. In one embodiment, the template-forming precursor liquid contains a polymer (e.g. PEO-PPO-PEO block copolymer) or mixture of polymers dissolved in a solvent that evaporates to form the desired mesoscale structure. In another embodiment, a template-forming precursor liquid forms a block copolymer from resins that undergo polymerization with micelles that coalesce to yield a mesoscale structure. The micelles can be produced from a long-chain surfactant. The template-forming precursor liquid reacts and/or dries to provide a mesostructured matrix. The wafer is heated to selectively evaporate solvent from the template-forming precursor liquid, leaving a mesostructured template on the substrate.

After the template is formed, a silica-forming precursor liquid may be introduced to form a mesoporous silica compound. Alternatively, this precursor material may be introduced earlier, together with all other components of the precursor layer. Examples of suitable silica-forming compounds include TEOS, tetramethoxysilane (TMOS), an organic alkoxysilane such as methyl triethoxysilane (MTEOS), methyltrimethoxysilane (MTMOS), dimethyldimethoxysilane (DMDMOS), dimethyldiethoxysilane (DMDEOS), a bridged

siloxane such as bis-triethoxysilylethane (BTEOSE) or bis-triethoxysilylmethane (BTEOSM), a cyclic siloxane such as tetramethylcyclotetrasiloxane (TMCTS), octamethylcyclotetrasiloxane (OMCTS) and mixtures of these precursors. These compounds are dissolved in a solvent to form the silica-forming precursor liquid. In one example, TEOS is dissolved to a 2% by weight concentration in a supercritical carbon dioxide solvent. Alternatively, where mesoporous metal oxides are desired, a metal-organic compound may be used where the metal-organic compound is compatible with the deposition chemistry. For example, metal alkoxides may be used with or without sol-gel forming acid catalysts. Compatible liquid solvents such as alkanes, cycloalkanes, and carboxylic acids may also be used to adjust the viscosity and/or vapor pressure of the silica-forming precursor liquid.

The resulting film will be an ordered mesoporous precursor layer suitable for applying methods of the present invention.

In another approach, a non-ordered porous precursor film is formed from a porogen that does not necessarily form an ordered arrangement of the type produced by amphiphilic self-assembly with block copolymers. In one example the precursor film is formed by co-deposition of porogen and dielectric material as by a PECVD process. Frequently, in such processes, the porogen is a hydrocarbon. The porogen may either be a separate molecule delivered simultaneously with the structure-forming precursor, or it may be covalently bonded to the precursor molecule. The structure-forming precursor and the porogen are delivered to the PECVD chamber and deposited on the wafer.

In a second step the porogen is removed to generate a porous film. The porogen removal step may be performed *in situ* in the same chamber or in a separate module or station. The porogen may be removed by a variety of methods including thermal degradation, exposure to UV radiation, exposure to e-beam or microwave energy. If thermal degradation is employed as the porogen removal step, the temperature of the wafer during the deposition process should be low enough to prevent the vaporization of the porogen, typically <250 C, and often as low as room temperature. Then, in the second step, the film is heated, typically to about 400 C, and the porogen either decomposes or vaporizes and is removed from the film, leaving behind voids. It is also possible to use higher wafer temperatures during the deposition process and then use UV radiation, e-beam or microwave methods to remove porogen. Methods of the present invention may be applied to either an as deposited film with the porogen still intact or after it has been partially or completely

removed by any of various methods such as those listed above (i.e., thermal degradation, UV radiation, e-beam or microwave exposure).

Note that this invention can be employed to form porous versions of many different materials, not just silicon oxides and silicates. Examples include metal oxides (e.g., oxides of Zr, Ti, Al and V), mixed metal oxides (e.g., superconducting perovskites such as the Y-Ba-Cu-O material), metals (e.g., Cu, Pt, Pd, and Ti), mixed metals, elemental semiconductors (e.g., Si, Ge, and C), compound semiconductors (e.g., III-V semiconductors such as GaAs and InP, II-VI semiconductors such as CdS, and IV-VI semiconductors such as PbS). Appropriate precursors will be apparent to those of skill in the art. As an example, many metal alkoxides are suitable metal oxide precursors.

Methods of the invention involve removing porogen material from a precursor layer using a plasma. When the porogen is removed, the dielectric regions of the precursor layer remain intact on the substrate leaving a dielectric matrix, sometimes referred to as a "dielectric backbone." These terms will be used interchangeably herein. Methods also involve "capping" hydrophilic regions in the dielectric matrix using a "silanol capping" agent. Details for implementing two preferred embodiments will now be described.

EMBODIMENT 1: PLASMA POROGEN REMOVAL AND *in situ* SILANOL CAPPING

Figure 1A is a flowchart summarizing aspects of a first embodiment of the invention. First, as indicated at block 101, a substrate with a deposited precursor layer is provided. As described previously, the precursor layer may be an ordered or mesoporous precursor layer or it may be a non-ordered precursor layer. In preferred embodiments, the precursor layer is an ordered mesoporous layer comprising template porogen and a silicon-containing dielectric phase which will become the dielectric matrix once the porogen is removed. In cases wherein a mesoporous precursor layer is used, this process is called "detemplating."

Next, one of various suitable plasma techniques is used to 1) remove at least a portion of the porogen material from the precursor layer and to 2) protect or "cap" hydrophilic portions of the dielectric matrix using a "silanol capping" agent. See 103. For removing porogen, any suitable plasma method that can cause the breakdown of the organic components of the porogen material may be used. The plasma power source can be either high frequency, low frequency or a combination of the two. In general, a high frequency

power component accelerates the dissociation of chemical species in the plasma while a low frequency power component emphasizes the bombardment effect to the substrate. In one example, the high frequency plasma source has a frequency of 13.5 MHz while the low frequency source is 400 kHz. Note that other porogen removal methods, such as thermal degradation, UV exposure, microwave exposure, electron beam exposure, supercritical processes, volatilization and solvent extraction, have been described in US Patent Application No. 10/404,693, which is incorporated in its entirety herein. One advantage of using plasma exposure techniques is that they can be conducted at relatively low temperatures and/or for relatively short times compared to, for example, thermal degradation techniques.

It has been found that a reducing plasma, usually comprising hydrogen and nitrogen, is effective for removing porogen without damaging the dielectric backbone. However, use of nitrogen can result in incorporation of nitrogen into the dielectric layer, which can cause later process integration issues. For example, if a photoresist is deposited thereon, the nitrogen may react with the photoresist to produce problematic "mushroom" structures. Oxidizing plasmas, however, have been found to attack and cause damage to the dielectric backbone. To address this problem, experiments with oxidizing plasma using less aggressive conditions (e.g., using milder oxidants such as CO_2) have been preformed and have been shown to create less damage to the dielectric backbone. Results from some of these experiments are described later.

In this first embodiment, porogen removal and silanol capping occur simultaneously using a single plasma. That is, the plasma comprises agents for removing porogen as well as silanol capping agents. In general, a silanol capping process helps to stabilize the porous dielectric matrix. The silanol capping agent can replace or protect the polar, hydrophilic hydroxyl (-OH) groups within the dielectric matrix with non-polar groups (e.g., alkyl groups), thereby rendering the film hydrophobic and allowing it to maintain a low overall dielectric constant, even when exposed to ambient moisture. Technically, silanol cappng in this context involves removing an acidic proton to form SiO- then protecting it as a silyl ether. Silanol capping may also involve tying up "dangling bonds," reactive unpaired valence electrons. As used herein, the term "silanol capping" and variations thereof refer broadly to any processes that involve replacing or protecting hydroxyl groups, dangling bonds, and other reactive or hydrophilic groups with hydrophobic groups.

Many silanol capping agents are suitable for this invention. Examples include, but are not limited to, disilazanes such as hexamethyldisilazane (HMDS), chlorosilanes such as

trimethylchlorosilane, aldehydes such as acetaldehyde, alkylsiloxanes such as dimethyldimethoxysilane (DMDMOS), and cyclic siloxanes such as TMCTS or OMCTS. If HMDS is used, for example, the SiO- groups will be protected with $Si(CH_3)_3$ groups forming $SiOSi(CH_3)_3$ moieties within the film.

5   In preferred embodiments, the silanol capping agent is introduced into a plasma that already has porogen removal agents. Note that the silanol capping agent may also act as a porogen removal agent itself. For example, HMDS may be injected into a H_2/N_2 containing plasma. The HMDS may be injected with or without a carrier gas. If a carrier gas is used, it is preferably an inert gas such as argon or helium. Other gases including nitrogen or

10   hydrogen or gas mixtures may also be used. The H_2/N_2 and HMDS plasma contacts a heated wafer to remove porogen and form methylated surface groups. The relative amounts of H_2/N_2 can vary. In one example, the plasma contained approximately 90% nitrogen and 10% hydrogen. Preferred wafer substrate temperatures range between about 100 and 450 degrees Celsius, more preferably between about 200 and 400 degrees Celsius. Plasma

15   exposure times can vary broadly depending upon plasma composition and other process parameters, but usually range between about 1 and 30 minutes. In one example, a H_2/N_2 and HMDS plasma exposure of the dielectric matrix for a period of between about 1 and 2 minutes was found to be effective. The optimum conditions for the plasma exposure including gas flow rates and the plasma source power depend on the configuration of the

20   plasma reactor. Plasma power ranges will depend significantly on the configuration and type of apparatus used and on the number of stations in the apparatus. In a specific example, a six showerhead Concept 2 SEQUEL™ tool from Novellus systems is used. Using the SEQUEL™ tool, preferred plasma source powers (for both high frequency and/or low frequency sources) range between about 100 and 2000 Watts distributed over six

25   showerheads, more preferably between about 150 and 500 Watts. Power ranges for either low or high frequency sources can vary depending upon a number of factors including tool configuration, number and size of wafers exposed and type of plasma(s) used (e.g., direct or downstream plasma). Preferred pressures range between about 1 and 20 Torr, more preferably between about 2 and 5 Torr. The dosage of silanol capping agent will also vary

30   broadly and depend upon a number of process parameters. In one example, HMDS was injected into the plasma at about 0.6 ml/min.

The porogen decomposition components and other byproducts may be removed by volatilization (*e.g.*, heating the wafer substrate and pumping away the residuals). Any suitable plasma reactor may be used. An example of a suitable apparatus is described later.

After the porogen is removed and the dielectric matrix is sufficiently treated, the process flow of Figure 1A is complete.

EMBODIMENT 2: PLASMA POROGEN REMOVAL FOLLOWED BY SILANOL CAPPING

Figure 1B is a flowchart summarizing aspects of a second embodiment of the invention. First, as indicated by block 105, a substrate with a deposited precursor layer is provided as described in the previous embodiment. Next, as indicated in block 107, the porogen is removed from the precursor layer using a plasma process. As in the previous embodiment, the plasma may be a reducing plasma or an oxidizing plasma. Plasma conditions and compositions are similar to those of the previous embodiment but without the silanol capping agent. As in the previous embodiment, the porogen decomposition components and other byproducts may be removed by volatilization (e.g., heating the wafer substrate and pumping away the residuals).

After porogen removal, the resulting dielectric matrix is exposed to a silanol capping agent, as indicated by process block 109. Note that this silanol capping process is preferably done without exposing the dielectric matrix formed at block 107 to ambient. This is to prevent ambient moisture from adsorbing onto the dielectric matrix, which will cause the overall k of the dielectric matrix to increase dramatically, as described previously. Again, the dielectric constant of water is about 80. Therefore, preferable methods include those in which the porogen removal and silanol capping processes are done in the same chamber or in which the vacuum is not broken between the two processes such as in a cluster type of apparatus. An example suitable apparatus is described later.

As in the previous embodiment, any suitable silanol capping agent can be used, including HMDS, chlorosilanes such as trimethylchlorosilane, aldehydes such as acetaldehyde, and alkylsiloxanes such as DMDMOS. Any suitable method for exposing the dielectric matrix to the silanol capping agent can be used. For example, the silanol capping agent may be introduced in vapor phase from a bubbler, or through a liquid delivery system. Alternatively, a supercritical solution process may be used. In preferred embodiments, the silanol capping agent is introduced to the dielectric matrix in a plasma. The plasma is preferably either a reducing plasma (e.g., H_2/N_2) or a mild oxidizing plasma (e.g., CO_2) such as described in the previous embodiment. As in the previous embodiment, the silanol capping agent may be introduced to the plasma with or without a carrier gas. The flow rate

of the silanol capping agent can depend upon a number of factors including the apparatus configuration and desired partial pressure to be achieved. In one example using the Novellus Concept 2 SEQUEL™ system, preferred flow rates of silanol capping agent ranged between about 0.2 and 2 ml/min. Preferred exposure times of the dielectric matrix to the plasma containing the silanol capping agent range between about 5 seconds and 20 minutes. Preferred plasma source powers range between about 150 and 500 Watts and preferred substrate temperatures range between about 100 and 400 degrees Celsius. Preferred chamber pressures range between about 2 and about 5 Torr.

After the dielectric matrix is sufficiently treated and the silanol capping processes is complete, the process flow of Figure 1B is complete.

APPARATUS

As mentioned previously, this invention is not limited to any particular plasma apparatus. Generally, the apparatus will include one or more chambers (sometimes referred to as process vessels) that house one or more wafers during porogen removal and silanol capping. A single chamber may be employed for both operations or separate chambers may be used. The one or more chambers maintain the wafer in a defined position or positions (with or without motion within that position, e.g. rotation, vibration, or other agitation) during porogen removal and silanol capping. The wafer may also be placed on a heating platen.

Importantly, the apparatus will protect wafers from exposure to ambient from the time when porogen removal begins until silanol capping is complete. This may be accomplished by a vacuum integration tool – such as a cluster tool – that provides multiple chambers all enclosed within or linked together via loadlocks to a larger vacuum chamber. Examples of such apparatus include the Concept 2 SEQUEL™, SPEED, SPEED-SEQUEL™, Concept 3 SEQUEL™ and VECTOR™ platforms from Novellus Systems, Inc. of San Jose, CA.

In a process environment, it may be beneficial to perform the porogen removal and silanol capping operations in the same apparatus as where the precursor layer is formed. As such, a multi-station tool for the various operations may be used. In some situations, the tool may include up to five chambers. For example, a first chamber may be reserved for template formation using a block copolymer. Second and third chambers are used to infuse dielectric

precursors into a mesoporous template formed in the first chamber. The precursors react to form a dielectric matrix in one phase of the template. Then, in a fourth chamber, the template-dielectric layer is detemplated. Finally, in a fifth chamber, the resulting dielectric matrix is silanol capped. In embodiments where the porogen removal and silanol capping occur simultaneously, the fourth chamber is used for porogen removal and silanol capping processes. If separate chambers are employed for porogen removal and silanol capping, the apparatus should be used in a manner that protects the dielectric matrix from exposure to moisture between the operations. In one embodiment, the entire apparatus is enclosed in a vacuum compartment. In another embodiment, the wafer path between the porogen removal and silanol capping chambers is maintained under vacuum.

Figure 2 is a block diagram depicting some components of a suitable plasma reactor for performing the invention. Note that this diagram depicts only a single plasma reactor chamber, which may be a part of a stand-alone single chambered apparatus or as one chamber of a multi-chambered apparatus as described above. Although various details of the apparatus have been omitted for clarity's sake, various design alternatives may be implemented. Therefore, the present examples are to be considered as illustrative and not restrictive, and the invention is not to be limited to the details given herein, but may be modified within the scope of the appended claims.

As shown, a reactor 201 includes a process chamber 203, which encloses components of the reactor and serves to contain the reactant gases and provide an area to introduce the reactant gases to substrate 209. In one example, the process chamber walls are made from aluminum. Within the process chamber, a wafer pedestal 207 supports a substrate 209. The pedestal 207 typically includes a chuck 208 to hold the substrate in place during the deposition reaction. The chuck 208 may be an electrostatic chuck, a mechanical chuck or various other types of chucks as are available for use in the industry and/or research.

A heat transfer subsystem including lines 211 for supplying a heat transfer fluid to the pedestal 207 controls the temperature of pedestal 207. In some embodiments, the heat transfer fluid comprises water or another liquid. In other embodiments, the pedestal 207 is heated electrically. The reactant gases (i.e., the porogen removal gases and silanol capping agent), as well as inert gases (if used), are introduced individually into the reactor at tube 225 via inlet 217. A showerhead 227 may be used to distribute the gas flow uniformly in the process reactor. Note that the shape of showerhead 227 may vary with different apparatus configurations. In one embodiment, showerhead 227 is plate-shaped and situated above and

parallel to substrate 209. Showerhead 227 is preferably RF biased while tube 225, via inlet 217 and process chamber 203 are at ground potential. These conditions can be achieved, for example, by electronically isolating showerhead 227 using a ceramic casing (not shown) from other components of the apparatus. A vacuum pump (e.g., a turbomolecular pump or a mechanical pump) connected to outlet 219 can draw out gases between processes. Note that Figure 2 illustrates an apparatus where the substrate is directly exposed to plasma. In some embodiments, the plasma source is remote or downstream from the substrate. This downstream plasma source configuration is not shown.

As mentioned previously, embodiments of the invention may involve a supercritical process for introducing the silanol capping agent. An example of an appropriate supercritical apparatus is described, for example, in US Patent Application No. 10/404,693, which is incorporated in its entirety herein.

FTIR EXPERIMENTS

Figure 3 is a composite graph of four Fourier transform infrared (FTIR) spectra of a mesoporous silica films. All samples are composite films made from tetraethyl orthosilicate (TEOS) and methyl triethoxysilane (MTEOS) precursors using at least one of the porous film formation methods described in US Patent Application No. 10/404,693. The curve 301 represents the FTIR spectrum of a TEOS/MTEOS porogen-containing precursor film without treatment. Curves 303, 305 and 307 are spectra of TEOS/MTEOS precursor films taken shortly after treatment with plasma comprising H_2/N_2 only (no silanol capping agent), HMDS and DMDMOS, respectively. Process parameters for the treated films included plasma power of about 160 Watts distributed over six showerheads in a SEQUEL™ tool from Novellus, substrate temperature of about 400 degrees Celsius, pressure of about 2.5 Torr and with plasma exposure times of about 1 to 2 minutes. For the samples with silanol capping agents (see spectra 305 and 307), the dosage of silanol capping agent was about 0.6 ml/min.

As shown by comparing the pretreated film (curve 301) to the three treated films (curves 303, 305 and 307), all three types of plasma processes effectively remove porogen material. Specifically, curve 301 (untreated film) has peak 311, indicating the presence of CH_x groups from the hydrocarbon template, and a large peak 323, attributed to the CO ether linkages in the template along with some contribution from the SiO cage structures in the backbone. Peak 311 does not appear in the treated film spectra 303, 305 and 309. In addition, peak 323 is largely reduced in the treated film spectra 303, 305 and 309 as the

template is removed but the SiO remains. Note that the peaks that still exist at around 1100 cm^{-1} in the spectra of the treated films 303, 305 and 309, such as peak 325, are attributed to the presence of SiO groups from the backbone.

Note that in spectrum 301 of the untreated film a broad peak 313 and peak 317 are present and they do not appear in the treated films' spectra 303, 305 and 307. These peaks (313 and 317) are attributed to H_2O that the porogen removal process also removes. Note that since the spectra of these treated films were taken very shortly after the plasma porogen removal process, there is no noticeable presence of H_2O in the H_2/N_2 only (no silanol capping agent) spectrum 303. However, if an FTIR were taken of this sample (303) after the sample is exposed to ambient for some time, the spectrum would show a significant presence of H_2O and the dielectric constant, k, of the film would be significantly increased. This would not be the case for the samples of spectra 305 and 307, which were treated with plasma containing silanol capping agents and would therefore be resistant to H_2O adsorption and the drift in k would be much less.

Other identifiable peaks in the spectra of Figure 3 include peaks 309, 315 and 319 attributed to $SiCH_3$ groups and peak 321 attributed to the linear chain SiO_2 groups of the dielectric backbone, which are present in the untreated and treated films.

Figure 4 is a graph showing data generated from FTIR spectra of two TEOS/MTEOS precursor samples, one treated with a H_2/N_2 plasma and the other treated with a CO_2 plasma. Neither sample was treated with a silanol capping agent. The graph of Figure 4 shows the effect on films in using a reducing plasma (i.e., H_2/N_2) versus an oxidizing plasma (i.e., CO_2).

As mentioned previously, ordinarily using an oxidizing plasma is not considered an ideal method of removing porogen since an oxidizer can not only remove template material but also attack and remove silcon-bonded organic groups, such as $Si-CH_3$ groups in TEOS/MTEOS precursor films, that are part of the dielectric matrix backbone. Removing these silcon-bonded organic groups, as discussed previously, would result in dangling unsaturated Si- groups, which form hydroxyl groups and, which in turn make the dielectric matrix more susceptible to water adsorption. It was found, however, that weak oxidizing plasmas, such as a CO_2 plasma, can be used under low plasma power conditions without too much degradation of organic groups in the dielectric matrix backbone.

To illustrate this, Figure 4 is a graph showing the ratio of the FTIR peak intensity of $Si-CH_3$ to Si-O present in two TEOS/MTEOS precursor films treated with H_2/N_2 plasma and

CO_2 plasma as a function of treatment time. Each TEOS/MTEOS precursor film was formed using similar process techniques and parameters as used to create films of Figure 3. Conditions for the film treated with H_2/N_2 plasma were plasma power of about 160 Watts over six showerheads, H_2 partial pressure of about 2 Torr, N_2 partial pressure of about 0.5 Torr and substrate temperature of about 400 degrees Celsius. Conditions for the film treated with CO_2 plasma were plasma power of about 160 Watts, CO_2 pressure of about 2.5 Torr and substrate temperature of about 400 degrees Celsius. Other process parameters were the same as in the experiment described for Figure 3. FTIR analyses were performed on each film after 0, 2, 4 and 8 minutes of plasma exposure times. The intensities of the $Si-CH_3$ peaks as measured by FTIR spectra are direct indications as to the amount of silicon-bonded methyl groups in the dielectric matrix of the films. Each film is compared by using the ratio of the FTIR peak intensities of $Si-CH_3$ to $Si-O$ for each film. As shown by Figure 3, the $Si-CH_3$ to $Si-O$ FTIR peak intensity ratio for the plasma untreated films (at time = 0) was about 0.43. After about 4 minutes of plasma treatment, the $Si-CH_3$ to $Si-O$ peak ratio of both films remained above 0.40. However, after about 8 minutes of plasma treatment, the $Si-CH_3$ to $Si-O$ peak ratio of the film treated with H_2/N_2 plasma remained above .40 but that of the film treated with CO_2 plasma was reduced to about 0.32.

Thus, while the H_2/N_2 plasma was better at not damaging the $Si-CH_3$ bonds within the dielectric backbone, the CO_2 plasma was also shown to not substantially damage the $Si-CH_3$ bonds up to at least 4 minutes. These oxidizing conditions, therefore, may be used, for example, in instances where it is preferable to avoid incorporation of any nitrogen into the film. In addition, a mixture of H_2 and CO_2 can be used wherein film properties such as the dielectric constant and film hardness can be modulated by adjusting the relative amounts of H_2 and CO_2.

OTHER EMBODIMENTS

While this invention has been described in terms of a few preferred embodiments, it should not be limited to the specifics presented above. Many variations on the above-described preferred embodiments, may be employed. Therefore, the invention should be broadly interpreted with reference to the following claims.